THE OXIDATION OF ISOPROPYL ALCOHOL, ACETONE, AND BUTYL COMPOUND BY NEUTRAL AND ALKALINE POTASSIUM PERMANGANATE

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DISSERTATION

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE SCHOOL OF OHIO STATE UNIVERSITY

By

LILY BELL SEFTON

Columbus, Ohio
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THE OXIDATION OF ISOPROPYL ALCOHOL AND ACETONE WITH NEUTRAL AND ALKALINE POTASSIUM PERMANGANATE

LILY BELL SEFTON

The oxidation of organic compounds has occupied the attention of a great many investigators during the last sixty years. Practically all the early work was qualitative in character and was conducted in open systems so that the oxygen of the air had an opportunity to act in conjunction with, and thus modify the results of, the specific oxidizing agent used. In 1899, Castle and Loevenhart[1] oxidized formic acid with alkaline hydrogen peroxide solution at carefully controlled temperatures and then determined the final products quantitatively. Since that time the tendency has been toward definite conditions and quantitative measurements.

The work represented by this thesis is a continuation of the work already done by Evans and Day[2] on ethyl alcohol and by Evans and Adkins[3] on acetaldehyde, glycol and related compounds. It is presented in two divisions:

I. The oxidation of isopropyl alcohol by neutral and alkaline potassium permanganate. Four series of experiments were conducted—one at 25° C., one at 50° C., one at 75° C., and one at 100° C. Since isopropyl alcohol boils at a temperature much below 100° C. (B. P. 82.85° C.) the results from the experiments made at that temperature were very irregular—too irregular to permit of drawing conclusions from them. The alkalinity of the samples in each series varied from 0 to 85.12 grams of KOH per 1000 cc. of solution. Thirty grams of permanganate were used in each sample and the amount of alcohol solution necessary for reduction added at a regular rate. All the reaction products were determined quantitatively.

II. The oxidation of acetone. This was done in the same manner and under the same conditions as the oxidation of isopropyl alcohol. Since the boiling point of acetone is even lower than that of isopropyl alcohol (B. P. 56–57° C.) the results obtained from oxidations made at 100° C., were more irregular than those from isopropyl alcohol at the same temperature so were not used as a basis for any conclusions.

The purpose of the work was three fold:

I. To determine the relation of alkalinity to the character and amounts of the products of oxidation.

II. To determine the relation of temperature to the character and amounts of the products of oxidation.

[1] *J. Am. Chem. Soc.*, **21**, 262 (1899).

[2] *Ibid.*, **38**, 375 (1916).

[3] *Ibid.*, **41**, 1385 (1919).

III. To ascertain the mechanism of the reactions when isopropyl alcohol and acetone are oxidized.

I. THE OXIDATION OF ISOPROPYL ALCOHOL

1. Historical.

The amount of work which has been done on the oxidation of isopropyl alcohol is very small when compared with that which has been done on acetone and on the normal alcohols—ethyl alcohol and butyl alcohol. M. Berthelot[1] oxidized isopropyl alcohol with potassium chromate and sulfuric acid, obtaining only acetone, or, in the case of the more concentrated solutions, the acetone oxidation products. In 1887, Remsen and Emerson[2] found upon oxidizing a series of aromatic compounds containing alkyl side groups, that the isopropyl group was more easily oxidized by acid oxidizing agents than by alkaline oxidizing agents. Hetper[3] oxidized isopropyl alcohol and acetone with potassium permanganate in both acid (phosphoric) and alkaline solutions. He was unable to get a complete combustion of either of them in alkaline solution.

2. Experimental Part.

Materials. The isopropyl alcohol used was obtained from the Eastman Company. Four tests were made of its purity.

Boiling point. The results of this test were very unsatisfactory. The boiling point ranged from 81°–87° C. (B. P. from Olsen, 82.25° C.). For the series of experiments at 50° C. a sample of alcohol boiling between 82°–84° C. was used. Unfortunately this exhausted the supply on hand so that the material used for the 25° C. and 75° C. runs was from a new supply.

Specific gravity determinations. The first sample had a density of 0.8004, the second 0.7976 (Olsen—0.7898; 0.7960).

Test for water. Both samples gave a blue tinge very quickly to dehydrated copper sulphate.

Oxidation. The first sample (used at 50° C.) showed a yield of only about 93 per cent; the second sample (used at 25° and 75° C.) gave yields of from 82–87%. Isopropyl alcohol is known to be very hard to free from water.[4] It forms various hydrates readily. The formula $C_3H_8O.\frac{1}{2}H_2O$ represents 86.82 per cent of the anhydrous alcohol. The possible hydrate $2C_3H_8O.\frac{1}{2}H_2O$ represents 93.03 per cent. Since the recovery yield of the first sample when oxidized was so consistently 93 per cent and that of the second sample 87 per cent the results obtained were calculated

[1] *Am. Chem. Jour.*, **23,** 212 (1872).
[2] *Ibid.*, **8,** 262 (1887).
[3] *Jour. fur. anal. Chem.*, **50,** 355 (1911); **51,** 417 (1912).
[4] Erlenmeyer *Annalen,* **126,** 307; Linneman *Annalen,* **136,** 40.

on the assumption that the two lots of isopropyl alcohol were hydrates of the formulas to which their oxidation percentage yields correspond.

A 3 N solution of the alcohol was made up with CO_2-free water. Attempts to make a more dilute solution resulted in the formation of a white cloudy material. This milky—apparently colloidal—substance concentrated on top of the mixture. No explanation could be found in literature concerning such a formation. Whether it was due to some slight impurity in the alcohol or whether to the formation of a hydrate less soluble than the alcohol itself is supposed to be, is not known.

Potassium permanganate. Braun's product, 99.75 per cent pure, was used.

Water. Since the ordinary distilled water of the laboratory showed a faintly acid reaction (3 drops of KOH were required to produce a pink color with phenolphthalein in 100 cc.), carbon-dioxide-free water was used in making up every sample and solution used.

Potassium hydroxide solutions. Baker's brand, purified from alcohol, was used.

A 4.5 N solution was used for making the samples alkaline. The carbon dioxide content of this solution was determined from time to time. (0.0011–0.0012 g. carbon dioxide per cc.)

A $\frac{N}{10}$ solution was used for determining the acetic acid content.

Potassium permanganate solution.

A $\frac{N}{3}$ solution was used for determining the oxalic acid.

Phosphoric acid. An 85 per cent solution was used in the distillation of acetic acid.

Methods—Oxidation. Thirty grams of potassium permanganate (the equivalent of) were weighed out and placed in a wide-mouthed 2-liter flask. To this exactly one liter of the potassium hydroxide solution was added. The initial alkalinity of the solutions varied from 0.00 to 85.12 grams of the base per liter. The flasks were fitted immediately with a rubber stopper provided with a tube for the introduction of the reducing solution, a mercury seal through which ran a motor-driven stirrer, and a 25 cc. pipette for drawing up and examining the reaction mixture from time to time. The flasks were then placed in the bath and the delivery tube of each fitted to the tip of a burette containing the reducing solution. Because of the low boiling point of isopropyl alcohol, it was necessary to make the connection between the burette and the delivery-tube practically air-tight lest isopropyl alcohol be lost by volatilization. The volatility of the isopropyl alcohol made it necessary also for the end of the delivery tube to be placed well beneath the surface of the solution in the flask. Preliminary experiments showed that the contents of the flask came to the temperature of the bath in about half an hour. In cases where the temperature and the alkalinity

were low, no harm probably would have resulted from allowing the mixture to stand for a longer time but the permanganate in those samples whose temperature and alkalinity were high, showed a tendency to decompose if allowed to stand for some time so care was taken to make the first addition of alcohol within an hour at least, after the permanganate and alkaline solution had been mixed. One cubic centimeter of the alcohol solution was added every half hour until the color of the supernatant liquid showed that the end point was near. Then the solution was added drop by drop and at longer intervals of time until only a faint pink color could be seen. If this pink color persisted over night and could be discharged in the morning by the addition of two drops of alcohol solution, the titration was considered successful—if the pink color disappeared over night, a new sample was titrated. After the reaction was complete the mixture was filtered in a carbon-dioxide free atmosphere by means of the apparatus designed and described by Evans and Day,[1] the precipitate washed three times with cold water, and the solution made up to 2000 cc. with carbon-dioxide free water and kept in glass-stoppered bottles sealed with paraffin. In the case of the neutral solutions at 25° C. and 50° C., it was necessary to determine by preliminary experiments the approximate amount of alcohol needed and then to start with fresh samples adding the calculated amount, one cubic centimeter every half hour, allowing whatever time was necessary for the reaction to come to completion. The necessity for the addition of the alcohol in a regular manner will be discussed later.

Determination of carbon dioxide. One hundred cc. of the reaction mixture were used and the estimation made by the Foulk method;[2] the gas was absorbed in Liebig tubes and proper corrections made for the carbon dioxide content of the potassium hydroxide solution.

Determination of oxalic acid. One hundred cc. of the reaction mixture were treated with an excess of sulfuric acid (1:4), heated to 80° C. and titrated with standard potassium permanganate solution. In order to make sure that no material except the oxalic acid was being attacked, every fifth sample was evaluated by precipitating the oxalic acid with calcium acetate, filtering, dissolving the precipitated oxalate and titrating the solution with permanganate. The results obtained by the method of direct titration checked in every case very closely with those of the precipitation method.

Determination of acetic acid. Two hundred cc. of the samples were used for these determinations. Adkins[3] outlined a modification of the Stillwell and Gladding method for acetic acid and this procedure was

[1] *Loc. cit.*

[2] Foulk's "Notes on Quantative Analysis," 222.

[3] *Loc. cit.*

followed with fair success. Control experiments showed a recovery of 99.57 per cent of acetic acid but it was found necessary with the reaction solutions and especially with those containing a higher percentage of acetic acid to distil over more than 400 cc. as recommended by Adkins. The method finally adopted was this: Four hundred cubic centimeters of the distillate were collected, the carbon dioxide removed according to the method of Adkins and the sample titrated with potassium hydroxide solution using phenolphthalein as an indicator. Additional distillates of from 75–100 cc. were collected and titrated until the last distillate required not more than two drops of the alkaline solution to bring it to end point. Total volumes of from 500–800 cc. were collected before all the acetic acid was over. Blank samples containing 20 cc. of phosphoric acid showed that it was necessary to make a correction of 0.25 cc. of the hydroxide solution for each estimation made.

Determination of acetone. The Robineau-Rollins-Kebler method described later in this paper was used for the estimation of acetone in most of the samples. In those whose acetone content was very low qualitative tests were made with salicylaldehyde. A small piece of solid sodium hydroxide was placed in a test tube with 10 cc. of the test solution. To this a few drops of salicyladehyde were added and the mixture heated to 70° C. The appearance of a red ring indicates the presence of acetone. This test is very delicate.

3. Results.

The results are given in three ways—by (tables,) by ordinary curves and by logarithmic curves. All experimental results were calculated to 0.1 molar quantity of isopropyl alcohol and these calculated results plotted against the initial alkalinity of the samples. The tables show that 30 grams of permanganate consume a much smaller quantity of isopropyl alcohol than of acetone. The amount of alcohol oxidized varies inversely with the value of the initial alkalinity and with the temperature.

Acetone is found as a reaction-product in the two lower series in addition to oxalic, carbonic, and acetic acids. At 50° C. the amounts were so small that they could be tested for only qualitatively and none was found in samples of an alkalinity value above 2.12 g. KOH per liter. The acetone production, then, like that of acetic acid and carbon dioxide, grows less as the alkalinity increases, and like the acetic acid yield, diminishes with increasing temperature. Josef Hetper[1] explains "the imperceptible influence of temperature on the oxidation of both isopropyl alcohol and acetone" by saying that the CH_3 in each is probably oxidized immediately by alkaline permanganate.

[1] *Zeit. für anal. Chem.* **51**, 417 (1912).

ISOPROPYL ALCOHOL

No. of samples	No. g. KOH in sample	No. g. alcohol oxidized	No. g. C_2O_4 obtained	No. g. CO_2 obtained	No. g. CH_3COOH obtained	No. g. CH_3COCH obtained	% Carbon recovery	Calculated yields from 0.1 Mol. of $CH_3CHOH.CH_3$(6.0064 g.)			
								C_2O_4	CO_2	CH_3COOH	CH_3COCH_3
					Temperature —25° C.						
1.	0.00	2.615	1.774	1.864	1.224	0.120	99.29	4.080	4.287	2.815	0.276
2.	0.50	2.481	2.054	1.793	0.897	0.077	97.92	4.970	4.348	2.178	0.191
3.	1.06	2.421	2.520	1.705	0.591	0.055	97.93	6.247	4.222	1.465	0.136
4.	2.12	2.418	2.734	1.696	0.450	0.039	97.45	6.780	4.203	1.116	0.097
5.	3.18	2.326	2.871	1.628	0.350	0.014	97.77	7.407	4.189	0.903	0.036
6.	5.32	2.276	2.867	1.595	0.339	Traces	99.12	7.568	4.210	0.895	Traces
7.	10.64	2.297	2.877	1.612	0.300	Traces	97.75	7.526	4.217	0.784	Traces
8.	21.28	2.313	2.890	1.600	0.312	Traces	97.12	7.508	4.157	0.810	Traces
9.	85.12	2.238	2.877	1.588	0.345	Traces	101.70	7.40	4.262	0.926	Traces
					Temperature —50° C.						
1.	0.00	2.423	2.100	1.966	0.740	Traces	96.90	5.202	5.116	1.832	Traces
2.	0.50	2.360	2.533	1.862	0.421	Traces	96.26	6.438	4.734	1.068	Traces
3.	1.06	2.345	2.649	1.819	0.386	Traces	97.79	6.774	4.652	0.988	Traces
4.	2.12	2.308	2.794	1.741	0.322	Traces	98.05	7.263	4.524	0.834	Traces
5.	3.18	2.289	2.882	1.678	0.289		99.27	7.554	4.398	0.756	
6.	5.32	2.259	2.917	1.634	0.279		100.00	7.746	4.338	0.741	
7.	10.64	2.277	2.965	1.609	0.228		98.01	7.812	4.242	0.600	
8.	21.28	2.260	2.983	1.604	0.230		99.19	7.920	4.254	0.606	
9.	85.12	2.260	2.931	1.593	0.233		97.93	7.795	4.239	0.618	
					Temperature —75° C.						
1.	0.00	2.224	1.977	2.196	0.271		92.47	5.332	5.920	0.733	
2.	0.50	2.192	2.415	1.932	0.164		95.27	6.610	5.283	0.448	
3.	1.06	2.192	2.620	1.840	0.156		97.29	7.169	5.035	0.414	
4.	2.12	2.177	2.737	1.728	0.149		97.86	7.535	4.750	0.408	
5.	3.18	2.167	2.782	1.658	0.144		97.31	7.680	4.565	0.400	
6.	5.32	2.164	2.832	1.645	0.146		98.69	7.846	4.557	0.400	
7.	10.64	2.164	2.836	1.653	0.143		98.69	7.860	4.579	0.400	
8.	21.28	2.160	2.839	1.630	0.148		98.45	7.873	4.532	0.402	
9.	85.12	2.164	2.838	1.640	0.144		98.53	7.855	4.542	0.400	

Below is a comparison of the results of the oxidation of this iso-alcohol with those of ethyl alcohol[1] made under practically the same conditions.

1. Neutral permanganate produces from ethyl alcohol acetic acid only; isopropyl alcohol produces oxalic, carbonic and acetic acids, and, in samples oxidized at 25° C. and 50° C., acetone also. This fact is a very significant one and will be discussed later.

2. Samples of low alkalinity and temperature produce from isopropyl alcohol the four substances listed immediately above; under no conditions does ethyl alcohol yield anything save oxalic, carbonic, and acetic acids.

[1] Evans and Day: *Loc. cit.*

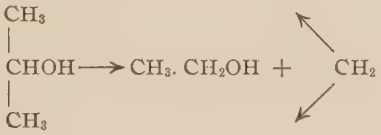
3. In the case of the ethyl alcohol the maximum (and minimum) acid yields correspond to a point where the alkali content of the samples is from 90 to 100 grams KOH per liter. When the iso-compound is oxidized, maximum and minimum acid yields are reached when the alkalinity is from 6 to 8 grams KOH per liter.

4. An increase in temperature produces a great deal more effect on the amounts of the products formed when ethyl alcohol is oxidized than when isopropyl alcohol is oxidized.

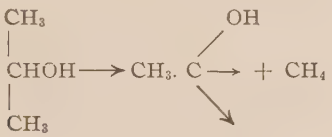
5. The rate of addition of ethyl alcohol affects neither the character nor amounts of the products formed; in the oxidation of isopropyl alcohol increased rate of addition results in increased amounts of oxalic acid.

4. Discussion of Results.

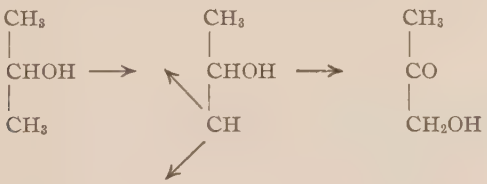
There are several possible ways in which the oxidation of isopropyl alcohol may take place.

1. 

Evans and Day have shown that when ethyl alcohol is oxidized under conditions precisely the same as those of this work, that no oxalic acid is obtained. Oxalic acid was one of the end-products of the oxidation of isopropyl alcohol—it could not have come from the methylene radical hence dissociation possibility one is excluded.

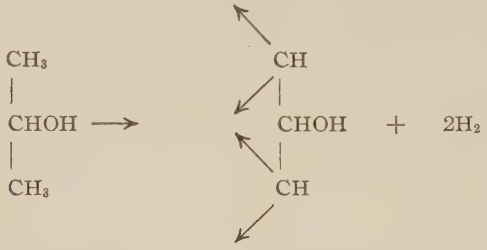
2. 

Frequent tests made during the oxidation of isopropyl alcohol showed that no methane was formed. Evidently therefore the alcohol does not dissociate in the manner suggested above.

3. 

[1] *Zeit. für anal. Chem.*, **50**, 355.

Denis[1] has proved that acetol does not, when oxidized with permanganate yield oxalic acid. This excludes possibility three.

4.


Such a dissociation does not provide for the formation of acetic acid and cannot therefore represent the manner in which isopropyl alcohol dissociate since acetic acid is one of the end-products of the oxidation of the isopropyl alcohol.

5.

The following facts are presented as evidence that the reaction takes place in the manner indicated by the above:

1. Berthelot[1] found only acetone when he oxidized isopropyl alcohol with dilute potassium dichromate.

2. By the principle of selective oxidation, the secondary alcohol group would be attacked before the very stable methyl groups.[2]

3. The curves for isopropyl alcohol follow very closely the curves for acetone.

4. Acetone in considerable quantity was found in the samples of isopropyl alcohol of lower alkalinity and temperature.

5. Since any acetone formed during the oxidation of isopropyl alcohol is in the nascent condition, one would expect it to be more readily attacked than when a solution of it is added to the permanganate solution. This is evidently the case: the difference in the case of oxidation is especially noticeable in samples of zero and low alkalinity at 25° C. and 50° C.

Further steps in the oxidation, that is, the mechanism of the acetone itself, will be discussed in the latter part of this paper.

5. Summary.

1. Isopropyl alcohol yields oxalic, carbonic, and acetic acids at all temperatures and degrees of alkalinity. Samples oxidized at 25° C. and 50° C. with neutral permanganate solution or permanganate solutions

[1] *Loc. cit.*

[2] Hetper: *Zeit. anal. Chem.*, **50**, 343–70.

of low alkalinity give acetone in addition to the three products named above.

2. The amounts of acetic and carbonic acids, and acetone formed are inversely proportional to the degree of alkalinity. The amounts of oxalic acid formed are directly proportional to the alkalinity.

3. The amounts of oxalic and carbonic acids formed are directly proportional to the temperature—the amounts of acetic acid and acetone are inversely proportional.

4. The logarithms of the amounts of oxalic, carbonic and acetic acids are within narrow limits—from 0.5 to 3.18 g. potassium hydroxide per liter—linear functions of the logarithms of the initial alkali concentration.

5. A comparison is made of the effect of neutral and alkaline permanganate on isopropyl alcohol and ethyl alcohol.

6. The maximum (and minimum) effects of variation in initial alkalinity are reached when the concentration of the alkali is from six to eight grams per liter of solution.

II. THE OXIDATION OF ACETONE

1. History.

The history of the oxidation of ketones may, without much exaggeration, be said to be the history of the oxidation of organic compounds, so often have they figured in the work of the various investigators. Pean de St. Gilles[1] who published one of the first papers on organic oxidations found, from the reaction of citric acid on an acid solution of potassium permanganate, a compound which proved identical with acetone. Concerning this compound he made a statement which has been a matter of dispute ever since: "I noted, not without surprise that it (the acetone) dissolved permanganate without alteration even at boiling temperature." He further said that "this fact makes it possible not only to establish the purity of the acetone but also to purify a commercial sample by destroying any oxidizable material in it." A discussion of this point will be taken up later.

A. Popoff[2] from the results of his own work and that of Kolbe, Wurtz, Erlenmeyer, Wanklyn and Butlerow made some valuable generalizations concerning the manner in which mixed ketones react when treated with an acid solution of potassium dichromate. The two best-known of these rules are (1), "When a ketone whose alcohol radicles are of the same series, but not isomeric, is oxidized, the carbonyl remains linked to the alcohol radical poorest in carbon;" and (2) "When the alcohol radicles of a ketone

[1] *Ann. Chem. et Phys. sec.* 3, **55,** 396 (1895).

[2] *Deut. Chem. ges. Ber.*, **4,** 720 (1871); *Ibid.*, **38,** 41 (1872); *Annalen*, **161,** 289 (1892).

belong to different series, the aromatic group will, upon treatment of the ketone with an oxidizing agent, remain with the carbonyl group giving rise to the corresponding acid while the aliphatic group will be further oxidized." Frequent exceptions to these rules have been found. Wagner[1] from ethyl-propyl ketone obtained butyric and acetic acids with propionic acid as the result of a secondary reaction and Glucksmann[2] working with pinacoline and alkaline permanganate obtained only trimethyl pyruvic and tri-methyl acetic acids. Hercz,[3] on the other hand, in his work on acetone confirms Popoff's rules as do Buchka and Irish[4] who, from acetophenone and alkaline potassium ferricyanide obtained only benzoic acid and carbon dioxide. Later, Evans[5] using the same materials, acetophenone and alkaline ferricyanide, obtained benzoylformic acid and benzoic acid. It is possible that in contradicting or confirming such general statements as Popoff's rules for the oxidation of ketones, too little account has been taken, up to date, of the fact that the differences in the oxidizing agents, in the media, in the temperature, etc. make marked differences in the character, as well as in the amounts, of the final products. The work of Josef Hetper[6] illustrates such differences admirably. He oxidized a large number of organic bodies, first with acid, and then with alkaline, permanganate and found that the results from the two series varied widely. (He used phosphoric acid in these experiments.)

Peter[7] used alkaline permanganate to oxidize acetothienone, $C_4H_3SCOCH_3$ and obtained β–Thiënylglyoxylic acid $C_4H_3SCO.COOH$ in addition to thiophenic acid C_4H_3SCOOH. When, however, he tried to obtain phenylglyoxylic acid in a similar manner from acetophenone, he failed. Claus and Stronmeyer[8] repeated the latter experiment and obtained the same results. Buchka and Irish[9] were able to produce small amounts of phenylglyoxylic acid by oxidizing acetophenone with alkaline ferricyanide but they, prejudiced evidently, in favor of Popoff's rule sought to explain this result by postulating a secondary reaction whereby benzaldehyde produced from a decomposition of acetophenone unites with unused acetophenone and hydrocyanic acid to form a cyanhydrin from which the keto-acid is produced. In 1890, Glucksmann[10] by treating acetophenone with alkaline permanganate at a low temperature obtained a good yield of

[1] *Jour. prakt. Chem.*, **44**, 257 (1892).
[2] *Monat. für Chem.*, **10**, 782 (1889).
[3] *Lieb. Ann.*, **186**, 257 (1877).
[4] *Ber.*, **20**, 386 (1887).
[5] *Am. Chem. Jour.*, **35**, 115 (1906).
[6] *Zeit. anal. Chem.*, **51**, 409 (1912).
[7] *Ber.*, **18**, 537 (1885).
[8] *Ibid.*, **19**, 230 (1886).
[9] *Loc. cit.* See also Evans—*Loc. cit.*
[10] *Monat. für. Chem.*, **11**, 246 (1890).

phenylglyoxylic acid. He attributed the failure of his predecessors to the fact that they did not use an excess of acetophenone. When an excess is used, the keto-acid which he regards as a product of the primary reaction, is kept from oxidizing further.

All of this work on acetophenone has a distinct, if indirect, bearing upon the question of the production of pyruvic acid from acetone. Fournier[1] was the first to present conclusive evidence that pyruvic acid was formed from acetone and alkaline permanganate altho Pastareau[2] three years before had found it in the reaction-product of acetone and alkaline hydrogen peroxide. Fournier showed that the yield of pyruvic acid was inversely proportional to the temperature and to the length of time required for oxidation, and that above 20° C. the pyruvic acid is oxidized completely to carbonic, oxalic, and acetic acids by alkaline permanganate.

Cochenhausen[3] and Witzemann[4] also have studied the action of alkaline potassium permanganate on acetone. Both worked at room temperature and both added the solid permanganate to the acetone in alkaline solution. Cochenhausen used an excess of the oxidizing agent and then decolorized with sodium peroxide. Witzemann's work and the results embodied in this paper show that unchanged acetone is likely to be present in the solution under the conditions of Cochenhausen's experiment, but Cochenhausen has not taken into account the fact that any such unchanged acetone will be attacked by sodium peroxide. Denis[5] oxidized with both neutral and alkaline permanganate acetone as well as acetol, mesoxalic acid, and other compounds directly related to acetone.

In general, there is a unanimity of opinion concerning the character of the products obtained from the oxidation of acetone by potassium permanganate, that is, that they consist of carbonic, oxalic, and acetic acids, with pyruvic acid if the oxidation takes place at a temperature below 20° C. Pastareau,[6] by using hydrogen peroxide in acid solution, obtained acetone peroxide, acetylcarbinol and pyruvic acid; but, with this one exception, not permanganate alone, but all oxidizing agents whether used in alkaline or acid medium, have yielded with acetone, acetic, carbonic, oxalic and pyruvic acids as final products. There is the widest divergence, however, in the quantitative results of the various oxidations but that is to be expected when one considers the differences in the conditions under which the various pieces of work were done.

[1] *Bull. Soc. Chim.*, **3**, 259 (1908).
[2] *Compt. Rend.*, **140**, 1591 (1905).
[3] *Jour. für prakt. Chem.*, **58**, 454 (1898).
[4] *Jour. Am. Chem. Soc.*, **39**, 2657 (1917).
[5] *Am. Chem. Jour.*, **38**, 561 (1907).
[6] *Loc. cit.*

2. Experimental Part.

Materials—Acetone. The acetone used had been made from the bisulfite addition compound. The purity of it was tested by four methods.

Boiling point. The results from this were not satisfactory. An oil bath was used and its temperature maintained between 65° C. and 70° C. The boiling point of the acetone ran from 53° C. to 58° C. (Olsen 56–57° C.)

Specific gravity determinations. These were made by a pyknometer standardized at 20° C. and gave an average value of 0.7924. (Olsen —0.7900.)

Anhydrous copper sulfate test. A sample in contact with anhydrous copper sulfate showed a distinct blue color after a few hours.

Titrimetric Evaluation. A. J. Field[1] after testing the various methods for the determination of acetone, recommended the Robineau-Rollins Method as modified by Kebler.[2] This method was used. Briefly the procedure is: Add to 20 cc. of an alkaline potassium iodide solution a measured sample of an aqueous acetone solution and from a burette run in while rotating the flask an excess of sodium hypochlorite solution. After one minute acidify the solution with hydrochloric acid and titrate with sodium thiosulfate solution.

By this method the acetone showed a purity of 97.53 per cent. 237.180 grams of it were weighed out from a weighing burette and made up to 1000 cc. with carbon dioxide-free water. This made an approximately 4 molar solution (1 cc. $\equiv$ 0.2313 g. acetone).

All other materials used were the same as those used for oxidation of isopropyl alcohol.

Methods—Oxidation. The acetone was oxidized in the same manner as the isopropyl alcohol.

Determination of acetone. In the samples of low alkalinity of the 50° C. series and in all of the samples of the 25° C. series excess acetone was found. This excess acetone was not a matter of chance in titrating; it seems to be necessary at lower temperature and alkalinities in order to bring about the complete reduction of the permanganate. The amount of excess varies inversely with the alkalinity and the temperature. Witzemann's[3] results support this statement. The Robineau-Rollins-Kebler method already described was used for the estimation of the unchanged acetone. In those samples in which the acetone content was very low the salicylaldehyde test was used.

Carbon dioxide, oxalic acid, and acetic acid were determined exactly

[1] *Jour. Ind. Eng. Chem.*, **10**, 552 (1918).
[2] *J. Am. Chem. Soc.*, **19**, 316 (1897).
[3] *Loc. cit.*

as described under isopropyl alcohol. In connection with the determination of oxalic acid a separate experiment was made to prove the action of permanganate on an acid solution of acetone. One hundred cubic centimeters of a 2 per cent solution of acetone containing 5 cc. of sulfuric acid (1:4) and heated to 80° C. remained pink for several hours after the addition of two drops of a tenth-normal permanganate solution.

3. Results.

The results of analyses are shown in three different ways: By tables; by ordinary curves; by logarithmic curves.

The tables of numerical data on the next pages are self-explanatory. Because of the difficulty encountered in titrating the permanganate solution to exactly the proper end point, many of the samples were checked three or four times. From the amounts of oxalic, acetic, and carbonic acids shown in columns 5, 6, and 7 were calculated the amounts of these substances which would be produced by 0.1 Mol. of acetone (5.805 g.) under the same conditions. These calculated results are given in columns 9, 10, and 11. They are used with the alkali concentrations in drawing the graphs and logarithmic curves.

Obviously the alkali concentration will be a constantly changing factor in these experiments and one must choose between defining it as the "initial concentration," the "final concentration" and the "average concentration" (calculated). If one desires to employ the latter term, he must take several factors into account:

(1) The volume of acetone solution tends to decrease the concentration of the alkali. With the exception of samples 1, 2, and 3 at 25° C. this volume is so small (10–15 cc.) that it might properly be disregarded. (2) The decomposition of the permanganate ($2KMnO_4 + HOH \longrightarrow 2KOH + 2MnO_2 + 3O$) is constantly increasing the alkali content of the samples. (3) As the various acids are produced part of the alkali is used for their fixation thus lessening the amount of free alkali. (4) Part of the alkali is, according to Morawsky and Stingl,[1] present in the brown sludge as $Mn_4KH_3O_{10}$. This point is regarded as open to argument, however, by later authorities. Considering the variability of these factors at any given points in the reaction a calculation of the "average alkali concentration" could be only a rude approximation. It was considered advisable, therefore to use the "initial concentrations" and these are given in column 1 of each series.

A peculiar situation exists in the "neutral" samples with reference to alkalinity. In the beginning they have a neutral reaction—at the end of the experiment a decidedly alkaline reaction. This means, of course, that a part of the general reaction took place, not in a neutral, but in an alka-

[1] *Jour. prakt. Chem.*, **18,** 82 (1878).

ACETONE

No. g. sample	No. g. KOH in sample	No. g. acetone introduced	No. g. unchanged acetone	No. g. acetone oxidized	No. g. C_2O_4 obtained	No. g. CO_2 obtained	No. g. CH_3COOH obtained	% carbon recovery	Calculated yields for 0.1 Mol. of Acetone (5.8036 g.) C_2O_4	CO_2	CH_3COOH
					Temperature 25° C.						
1	0.00	12.340	9.067	3.273	0.371	2.292	3.156	98.03	0.656	4.056	5.586
2	0.50	5.718	2.522	3.196	1.397	2.685	2.046	97.43	2.537	4.876	3.716
3	1.06	4.607	1.916	2.691	2.026	2.156	1.192	96.89	4.370	4.650	2.571
4	2.12	3.137	0.596	2.541	2.572	1.976	0.817	99.20	5.874	4.505	1.340
5	3.18	2.832	0.285	2.547	3.074	1.916	0.416	97.12	7.009	4.369	0.948
6	5.32	2.631	0.121	2.510	3.258	1.885	0.330	98.64	7.533	4.358	0.763
7	10.64	2.561	0.081	2.480	3.312	1.855	0.331	100.20	7.751	4.341	0.774
8	21.28	2.561	0.054	2.507	3.325	1.880	0.329	99.74	7.701	4.354	0.778
9	85.12	2.531	0.031	2.500	3.329	1.872	0.336	100.13	7.733	4.349	0.780
					Temperature 50° C.						
1	0.00	3.470	0.428	3.042	0.565	3.075	2.156	98.36	1.079	5.868	4.116
2	0.50	3.220	0.592	2.628	2.004	2.761	0.783	98.90	4.426	6.095	1.729
3	1.06	2.794	0.251	2.543	2.427	2.393	0.545	97.34	5.540	5.462	1.242
4	2.12	3.470	0.925	2.545	2.866	2.049	0.469	97.50	6.554	4.679	1.080
5	3.18	2.961	0.434	2.527	3.196	1.910	0.330	97.58	7.314	4.384	0.758
6	5.32	2.535	0.000	2.535	3.342	1.915	0.291	98.66	7.651	4.399	0.662
7	10.64	2.487	0.000	2.487	3.419	1.871	0.241	99.72	7.982	4.371	0.560
8	21.28	2.494	0.000	2.494	3.388	1.900	0.238	99.42	7.906	4.422	0.553
9	85.12	2.487	0.000	2.487	3.410	1.897	0.242	100.80	7.958	4.428	0.543
					Temperature 75° C.						
1	0.00	2.644	0.0	2.644	0.910	3.400	1.064	97.92	1.998	7.466	2.344
2	0.50	2.463	0.0	2.463	1.892	2.925	0.429	97.33	4.562	6.894	1.011
3	1.06	2.465	0.0	2.465	2.242	2.759	0.382	99.23	5.275	6.495	0.900
4	2.12	2.457	0.0	2.457	2.752	2.322	0.363	99.98	6.502	5.483	0.856
5	3.18	2.461	0.0	2.461	3.132	2.068	0.308	100.90	7.388	4.877	0.725
6	5.32	2.463	0.0	2.463	3.299	1.928	0.273	100.50	7.775	4.542	0.643
7	10.64	2.463	0.0	2.463	3.394	1.918	0.210	100.40	7.977	4.521	0.493
8	21.28	2.452	0.0	2.452	3.393	1.896	0.205	100.30	8.020	4.485	0.483
9	85.12	2.457	0.0	2.457	3.388	1.909	0.204	100.10	8.007	4.513	0.481

line medium. Adkins[1] found in oxidizing acetaldehyde in "neutral" solution that the solution was faintly acid at the end of the reaction due to the presence of carbon dioxide. Chapman and Smith[2] in a report of their work with ethyl alcohol and neutral permanganate go into detail concerning this change of reaction.

"The fact is, the neutral permanganate is, by the abstraction of 1 equivalent of oxygen in the presence of water, converted into 1 equivalent of

[1] *Loc. cit.*

[2] *Jour. Chem. Soc.*, **20**, 301 (1867).

manganate of hydrated manganic acid.....which at once splits up into binoxide of manganese and oxygen. From this it appears that two-thirds of the available oxygen of the permanganate may be removed without in any way affecting the neutrality of the solution. But as in this reduction acids are formed, an even larger quantity of oxygen may be removed from the permanganate before the solution has become really alkaline..... We have, in fact, a most complicated series of reactions; first, action in a neutral solution; second, action in a..... possibly.....acid solution, and third, action in a alkaline solution." These authors suggest the use of manganate rather than permanganate as a means of obtaining a more regular set of conditions.

The character of the manganese sludge and its mode of formation was much the same as described by Day.[1] In the samples of high alkalinity the manganese oxides were reddish brown and had a tendency to be flocculent; in the samples of low alkalinity the sludge formed more slowly and was an exceedingly fine, almost black powder. In the neutral solutions at 25° C. and 50° C. the oxides appeared to be present as colloidal matter for as long as two days—then gradually precipitated out.

Adkins[2] speaks of the fact that in the faintly acid solutions resulting from oxidations in a "neutral" medium, large masses of organisms appeared after a few days. The same thing was observed in occasional samples of this work but seemed to be a freak effect—that is, the growths were as likely to develop in a sample of high, as of low, alkalinity and many of the samples showed no trace of them after standing for weeks. Moreover, such growths seemed to have no effect upon the content of the samples in which they developed: analyses made several weeks apart checked closely.

Evans and Day[2] and Evans and Adkins[2] proved that the rate of the addition of the reducing agent made no difference upon the amounts of the reducing solution required nor upon the amounts of the oxidation products obtained. Preliminary experiments showed that this was not true of acetone. Samples to which the acetone solution had been added rapidly yielded more oxalic and less carbonic acid than samples to which the solution had been added slowly. To test the point three experiments were made at 75° C., each containing 5.32 g. of alkali. To the first one cc. of the reducing solution was added every fifteen minutes; to the second, one cc. every thirty minutes; and to the third, one cc. every sixty minutes. The differences between the amounts of acetone required were well within the limit of experimental error but the amounts of oxalic acid which they yielded varied appreciably. The first gave 0.906 g., the second 0.898 g.

[1] Day: Thesis, 1916, p. 36.

[2] *Loc. cit.*

and the third 0.879 g. This evidence is, of course, too scanty to serve as a basis for any general conclusions but taken in connection with previous observations and with the very significant results obtained with butyl alcohol,[1] it indicates the advisability of a regular addition of acetone. The rate already given—one cc. every half hour—was used throughout the work of this paper.

No attempt was made to go further with the problem of the rate of reaction. That constitutes a field in itself. Some work has already been done on it. Dreyfus[2] working in acid solution and using ethyl alcohol as a standard, determined the rates of reaction for several organic substances.

Castle and Loevenhart[3] oxidized formic aldehyde with alkaline hydrogen peroxide in order to determine the rate of reaction. A more ambitious piece of work was undertaken by C. W. R. Powell.[4] He studied the rate of reaction of sucrose with alkaline, acid, and neutral permanganate. In acid solution his results indicated a bi-molecular reaction although he found that the velocity coefficient increased during the course of the reaction.

Figs. 2, 3, and 4 show the products from oxidations made at 25° C., 50° C., and 75° C., respectively, plotted against initial alkali concentrations. Fig. 5 shows oxalic acid yields from oxidations at the three temperatures given; Fig. 6 the carbonic acid yields and Fig. 7 the acetic acid yields. Logarithmic curves corresponding to those are given in Figs. 8, 9, and 10.

Reference has been made to the fact that there is a difference of opinion concerning the action of neutral permanganate solution on acetone. Sometime after St. Gilles[5] made the statement that acetone was unaffected by permanganate solution, F. Sachs[6] used boiling acetone as a medium for affecting the oxidation of certain benzyl compounds with permanganate. Martines[7] used a solution of permanganate in acetone for the oxidation of menthones. The most recent published work on acetone[8] confirms the findings of St. Gille, Sachs, and Martines. Witzemann added solid permanganate to a neutral solution of acetone and allowed it to stand for several weeks. At the end of that time there was no indication of action between the two substances.

[1] Supplement to this thesis.
[2] *Compt. Rend.*, **105,** 523.
[3] *J. Am. Chem. Soc.*, **21,** 262 (1899).
[4] *Jour. Proc. Roy. Soc.* N. S. Wales, **48,** 11, 223.
[5] *Loc. cit.*
[6] *Ber.*, **34,** 497 (1904).
[7] *Ann. Chem. et phys., Ser.* 8, **3,** 82 (1904).
[8] Witzemann, *Loc. cit.*

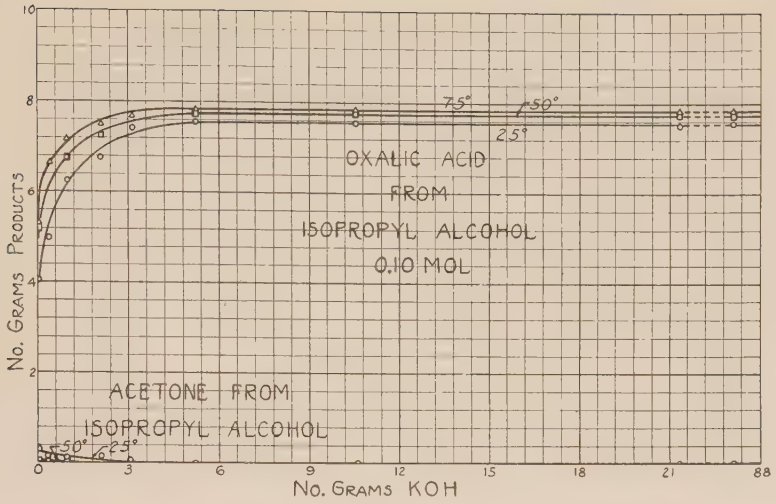

No. Grams Products
No. Grams KOH
75°
50°
25°
OXALIC ACID
FROM
ISOPROPYL ALCOHOL
0.10 MOL
ACETONE FROM
ISOPROPYL ALCOHOL
50°
25°

Fig. 1

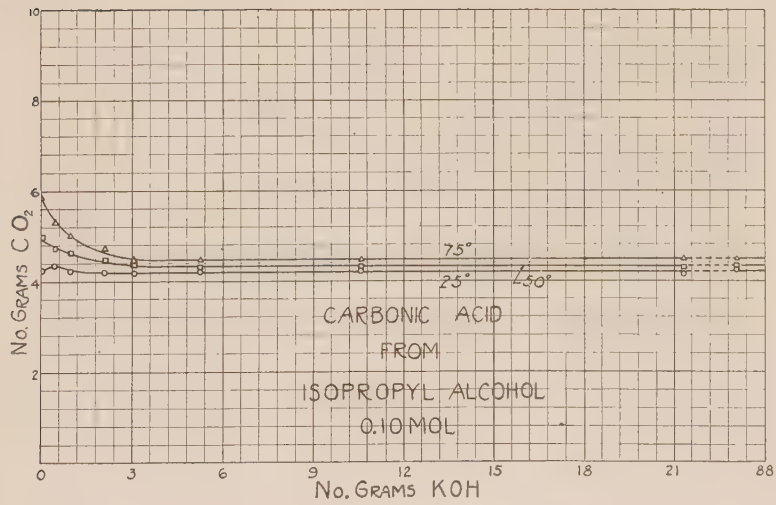

No. Grams CO_2
No. Grams KOH
75°
25°
50°
CARBONIC ACID
FROM
ISOPROPYL ALCOHOL
0.10 MOL

Fig. 2

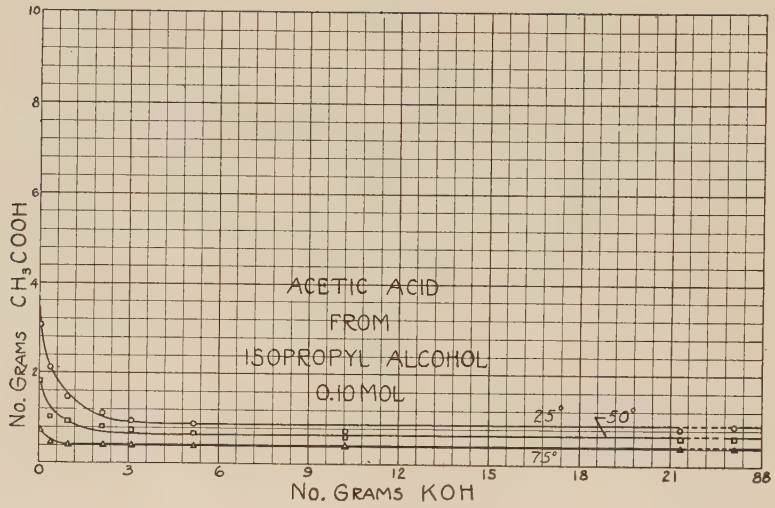

ACETIC ACID
FROM
ISOPROPYL ALCOHOL
0.10 MOL
25°
50°
75°
No. Grams CH3COOH
No. Grams KOH
0
3
6
9
12
15
18
21
88
2
4
6
8
10

Fig. 3

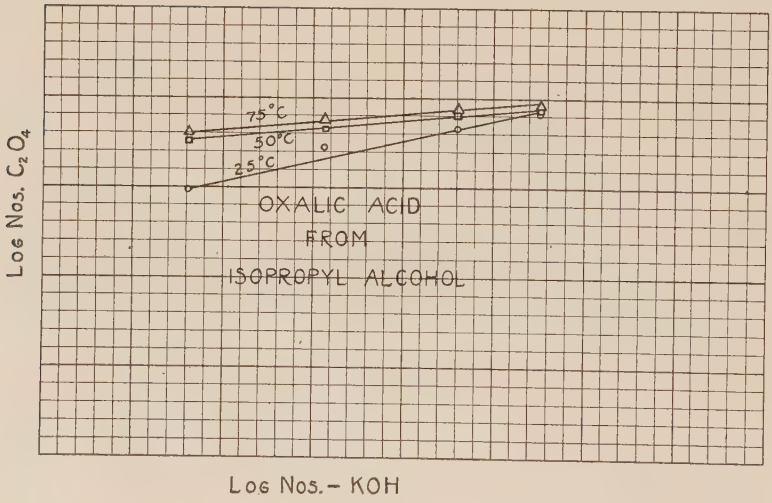

75°C
50°C
25°C
OXALIC ACID
FROM
ISOPROPYL ALCOHOL
Log Nos. C2O4
Log Nos.- KOH

Fig. 4

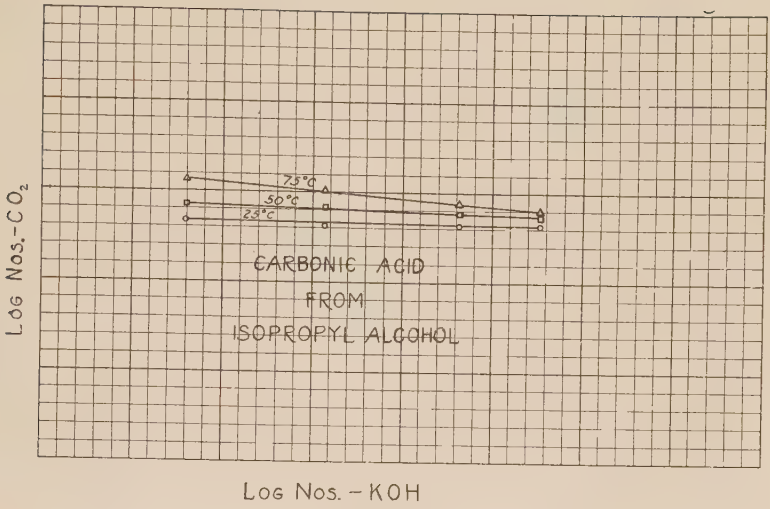

75°C
50°C
25°C
CARBONIC ACID
FROM
ISOPROPYL ALCOHOL
Log Nos. - CO_2
Log Nos. - KOH

Fig. 5

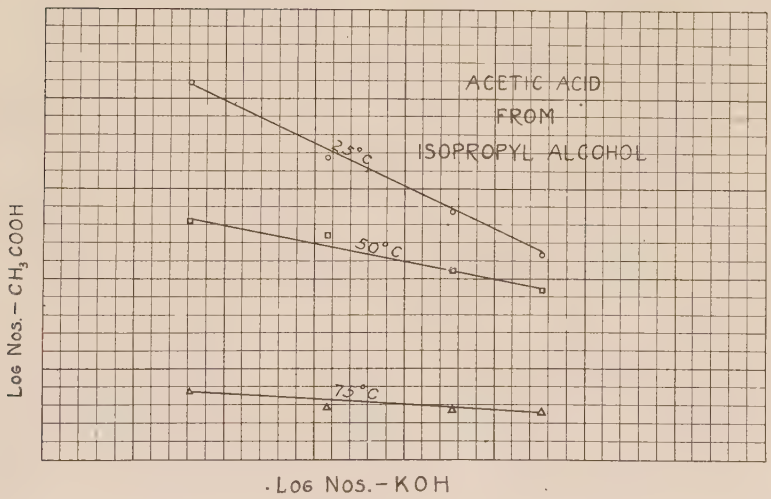
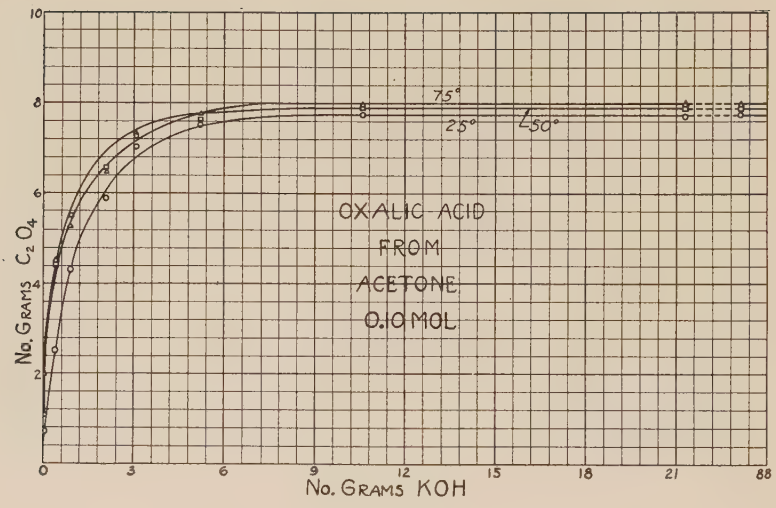

ACETIC ACID
FROM
ISOPROPYL ALCOHOL
25°C
50°C
75°C
Log Nos. - CH_3COOH
Log Nos. - KOH

Fig. 6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No. Grams KOH
75°
50°
25°
OXALIC ACID
FROM
ACETONE
0.10 MOL

Fig. 7

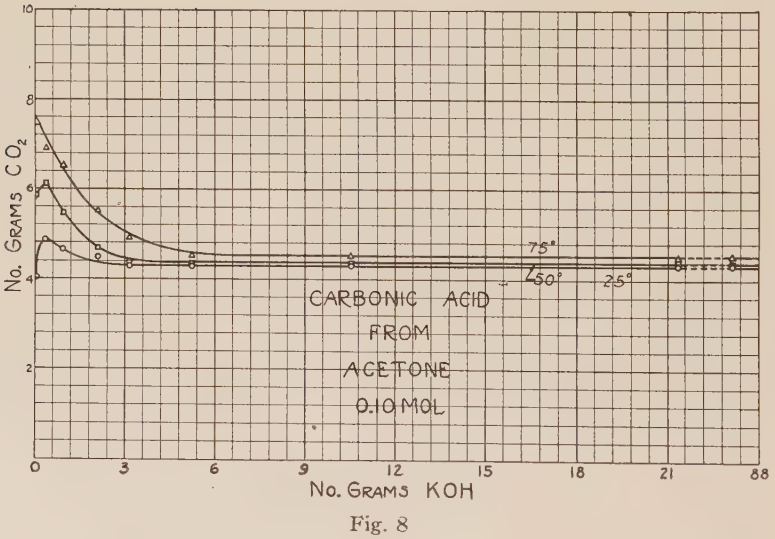

No. Grams CO_2
No. Grams KOH
75°
50°
25°
CARBONIC ACID
FROM
ACETONE
0.10 MOL

Fig. 8

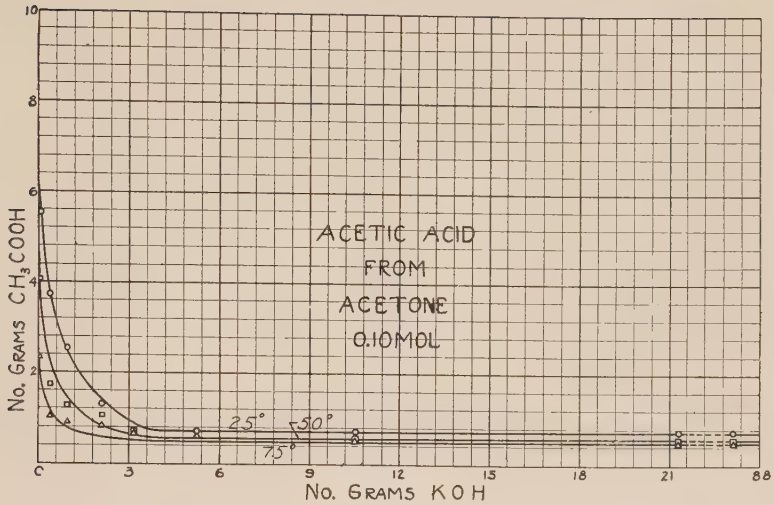

ACETIC ACID
FROM
ACETONE
0.10MOL
25°
50°
75°
No. GRAMS CH_3COOH
No. GRAMS KOH
0
3
6
9
12
15
18
21
88
2
4
6
8
10

Fig. 9

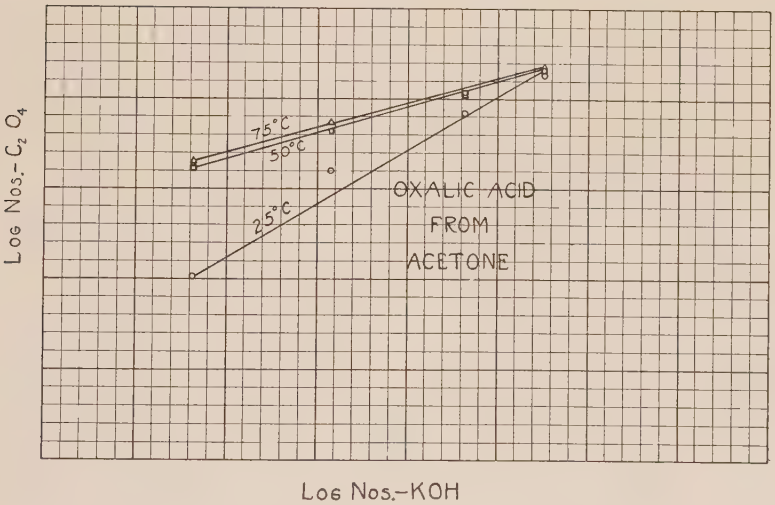

75°C
50°C
25°C
OXALIC ACID
FROM
ACETONE
Log Nos.- C_2O_4
Log Nos.-KOH

Fig. 10

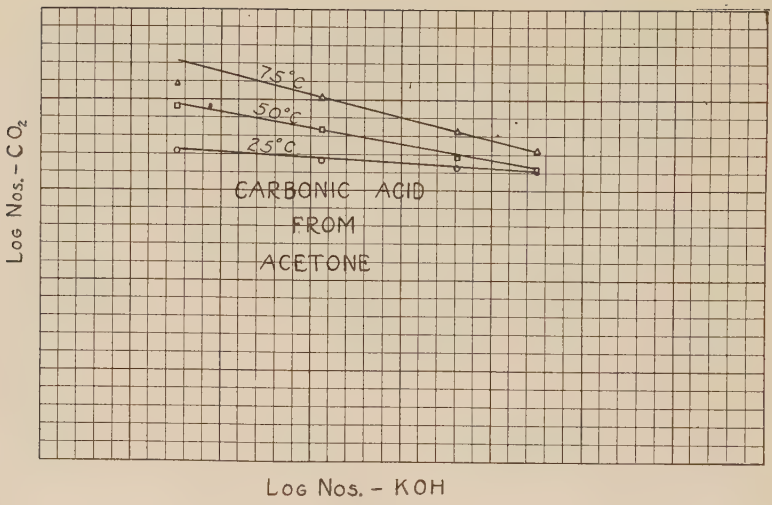

75°C
50°C
25°C
CARBONIC ACID
FROM
ACETONE
Log Nos. - CO_2
Log Nos. - KOH

Fig. 11

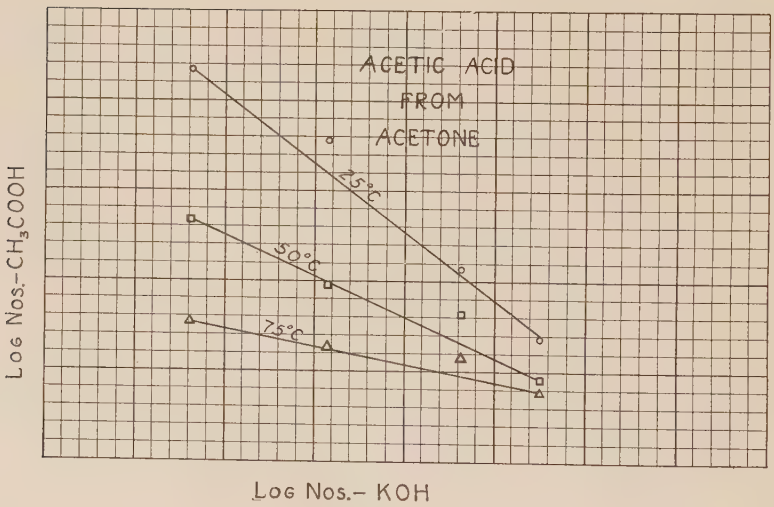

ACETIC ACID
FROM
ACETONE
25°C
50°C
75°C
Log Nos. - CH_3COOH
Log Nos. - KOH

Fig. 12

Hercz,[1] on the other hand found that acetone was oxidized to acetic acid and carbon dioxide by neutral permanganate. Fournier[2] says that "pure acetone is oxidized very slowly by a neutral solution of permanganate," and Denis,[3] upon heating acetone with an excess of neutral permanganate at 50°–55° C., obtained oxalic, carbonic, and acetic acids in quantitative amounts. The work of this paper is in accordance with the results obtained by the last named investigators. At no time and at no temperature was there any doubt that the acetone was being attacked altho the reaction at all three temperatures was very much slower than that of samples initially alkaline and at 25° C. and 50° C. and excess of the acetone was necessary to bring about complete reduction. In the neutral sample at 25° C. this excess of the acetone was necessary to bring about complete reduction. In the neutral sample at 25° C. this excess amounted to nearly three times the amount actually consumed and four days were required for complete reduction. In another sample at 25° C. the excess was approximately equal to the amount used, but twelve days were required for complete reduction. The oxalic acid content of the two reaction-products checked very closely.

There are several possible reasons for the varying results obtained by different investigators:

1. The action observed by Hercz,[5] Fournier,[3] and the author of this paper may be due to the fact that the acetone used contained some impurity which initiated a slight decomposition of the permanganate thus establishing an alkaline condition. It seems hardly likely, however that St. Gilles, for instance, would be able to obtain a purer product than Hercz or Fournier.

2. Witzemann[3] added the solid permanganate a little at a time to a definite amount of acetone solution. In this work the acetone solution was added at regular intervals to a fixed amount of permanganate. That a difference in the order of addition of the reagents makes a difference in the quantitative results is shown in the supplement to this paper. It may be that this difference, in the case of acetone, is extended to a difference in the character of the products. Work testing this point is under way.

3. It happens sometimes that there are in certain laboratories minute quantities of bodies which exert a catalytic effect on a given reaction when these bodies are absent, the reaction goes on in an entirely different manner. Professor C. W. Foulk of this laboratory cites two examples of this which came under his personal observation—one which accounted for differences observed by Professor N. W. Lord of Ohio State University

[1] *Lieb. Am.*, **186,** 257 (1877).
[2] *Bull. soc. Chem.*, **3,** 259 (1908).
[3] *Loc. cit.*

and Doctor Cain of the Bureau of Standards and the other for differences observed by Ostwald and Bredig. Possibly the same explanation may serve as a reason for the differences in question.

4. Differences in the concentration of the reacting materials may account for the recorded differences in behavior. Sachs[1] and Martines[1] dissolved the permanganate crystals in pure acetone and found that it was without effect upon the acetone. Fournier[1] with a neutral solution of permanganate and pure acetone observed a slow oxidation. Hercz[1] also used a solution of permanganate and obtained an oxidizing action. Witzemann[1] on the other hand, noted no change when crystals of permanganate were added to an acetone solution, while Denis[1] and the author of this paper by using both the permanganate and the acetone in aqueous solution were able to oxidize the acetone. In view of this data it seems hardly likely that the dissociating action of water in itself initiates the action.

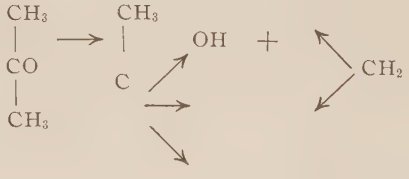
4. Discussion of Results.

Evans and Day[1] have summed up very completely the evidence which shows (1) that oxalic acid is not formed from acetates and (2) that carbonic acid is not formed from oxalates nor acetates under the conditions which obtained for the work of this paper. The tables and curves show that all three of these substances are formed when acetone is oxidized by either neutral or alkaline permanganate.

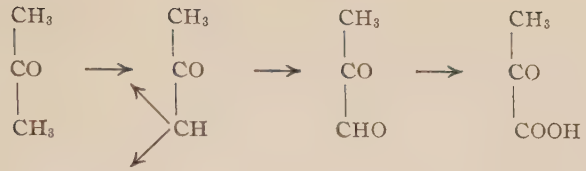
Effect of varying initial alkalinity.—1. As with isopropyl alcohol, the amounts of acetic and carbonic acids produced are inversely proportional to the initial alkalinity. 2. The amounts of oxalic acid vary directly with the alkalinity. 3. After the initial alkalinity has reached a value of six to eight grams per liter it produces a constant instead of a varying effect upon the production of the various acids.

For an explanation of these results it is necessary to consider the dissociation possibilities of acetone:

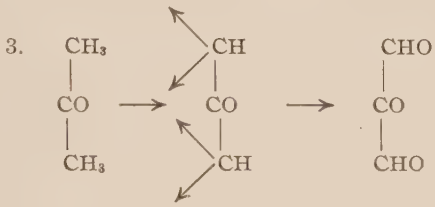
Such a dissociation does not provide for the formation of oxalic acid—a substance which is shown to be one of the end-products when acetone is oxidized.

1. 

[1] *Loc. cit.*

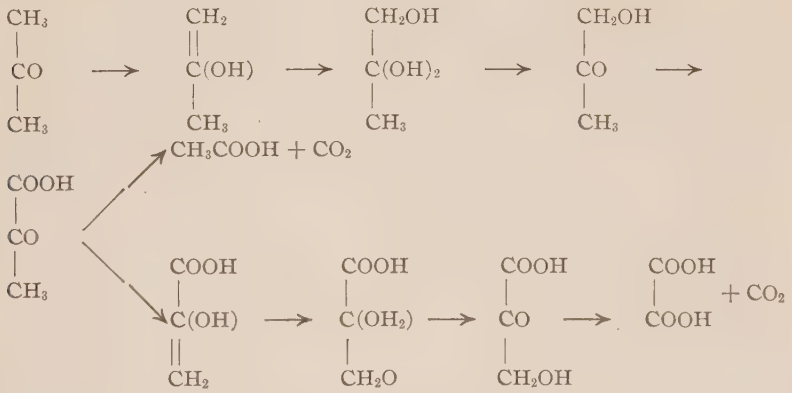
2. 

That pyruvic acid is formed by the oxidation of acetone is proven beyond a doubt by Fournier[1] and confirmed by both Denis[1] and Witzemann.[2] The last two investigators account for its production however by the enalization of acetone (see possibility 4).

3. 

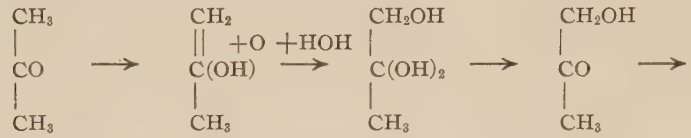
If acetone dissociated in this way no acetic acid would be formed, hence this possibility is excluded.

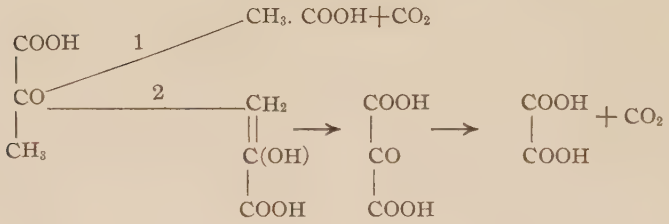
4. *Denis-Witzemann Reaction.*—Witzemann[3] on the basis of his own work and that of Denis[3] on acetone and related substances had presented the following as the probable mechanism for the oxidation of acetone by alkaline permanganate:



[1] *Loc. cit.*
[2] *J. Am. Chem. Soc.*, **739**, p. 2666.
[3] *Loc. cit.*

He calls attention to the fact that every step of this mechanism has been backed by experiment except the enolization of the pyruvic acid. Denis,[1] whom he cites as authority, worked mostly at room temperature and used samples whose initial alkalinity ranged from 0.0 to 30.0 grams KOH per liter. Assuming tentatively the correctness of this mechanism under such conditions let us consider the effect (1) of decreasing alkalinity; and (2) of increasing temperature.





Effect of Alkalinity.—An examination of the curves shows that in general, a decrease in the alkalinity produces an increase in the amount of carbonic acid produced.

Suppose the decrease in alkalinity shifted the reaction so that it followed entirely course 1—suppose it caused it to go entirely in the direction of 2—suppose it goes partly (any proportion) in one direction and partly in another: in any of the three cases, two molecules of carbonic acid would be produced respectively for every two of acetic or for every two molecules of carbonic acid or for every one molecule of oxalic and one of acetic, and that would mean a straight line for the carbonic acid provided the amounts of acetone used for the reduction of the sample were practically the same.

But the carbonic acid production in samples containing less than 7 grams KOH per liter when plotted against initial alkalinity, do not give straight lines and the differences in the amounts of acetone used are not nearly great enough to account for the curve which they make. It follows then that;

1. There is accompanying the Denis-Witzemann reaction, some other reaction that yields a larger proportion of carbonic acid *or* that

[1] *Loc. cit.*

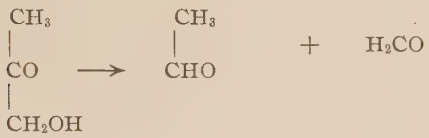
2. In samples of low alkalinity, some product of the Denis-Witzemann reaction is yielding carbonic acid *or* that

3. A combination of these two factors produces the effect observed.

In a piece of work recently completed at Ohio State University by O. C. Hoover, it has been shown when acetol in neutral solution is oxidized under the same conditions as those which obtained in this work, five-sixths of the carbon appeared in the form of CO_2, and further, that the amount of carbon appearing as CO_2 decreased with increasing alkalinity of the samples.

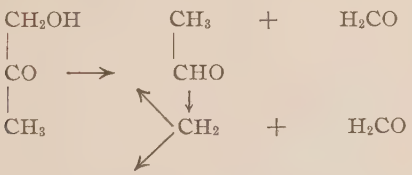
According to the Denis-Witzemann reaction acetol (which appears as the third product of oxidation) would yield only one-half of its carbon as CO_2. It is fairly certain then that in samples of acetone at low alkalinity, the reaction follows some other course than that indicated by "possibility 4."

Suppose acetol dissociated thus:

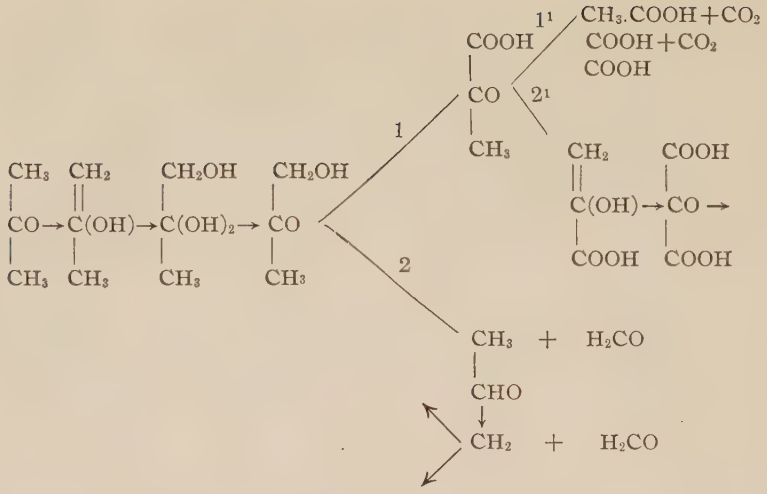


One-third of the carbon only could appear as CO_2 in this case. But if we conceive of at least a part of the $CH_3.CHO$ dissociating into methylene and formaldehyde:

then we shall have accounted for the large amounts of CO_2 formed. Such a dissociation of acetol does not provide for the production of oxalic acid and this is in accordance with experimental fact for Hoover obtained no oxalic acid from neutral samples of acetol. The fact that the CO_2 curve from acetol is practically the same as the CO_2 curve from acetone supports the assumption that there is accompanying the Denis-Witzemann reaction a side-reaction



and that this reaction is suppressed by increasing alkalinity as is to be expected since the substitution of the metals for hydrogen in compounds always tends to stabilize them. The complete mechanism may be represented as follows:



It may be that the excess of carbon dioxide in samples of low alkalinity is due to the fact that there is not, in the beginning of the reaction, sufficient alkali present to form normal salts with the oxalic and carbonic acids produced and that acid salts are formed. In that case, the acid oxalate would break down to CO_2 in the presence of permanganate. This tendency to form acid salts would naturally grow weaker as the alkalinity, initial and induced, became greater and the carbon dioxide production would fall off.

In the carbon dioxide curves at 25° C. and 50° C., there is a curious break between the neutral samples and the samples containing 0.5 g. alkali per liter. The most plausible explanation for this apparent irregularity is found by considering the fact that at these two temperatures neutral samples furnish very large amounts of acetic acid, with the substance of the paper from Chapman and Smith[1] quoted in the first part of this article: "we have then three sets of conditions—neutral solution, acid solution, and alkali solution." Is it not possible that the existence for even a short period, of acidity might suppress the formation of carbon dioxide?

There is another point to be considered in connection with this apparent irregularity. The crest of the break may occur at a point very much nearer the line of zero alkalinity than is indicated. No samples were estimated whose alkalinity lay between 0.0 and 0.5 g. KOH.

2. *Effect of temperature.*—A study of the curves—Figs. 5, 6, 7—indicates 1. That the general effect of increasing temperature is to send the Denis-Witzemann reaction in direction 2—that is, to increase the production of oxalic and decrease the production of acetic acid.

[1] *Loc. cit.*

2. That increasing temperature has an accelerating effect upon the speed of whatever factor or combination of factors produce carbon dioxide. If one accepts the modified Denis-Witzemann reaction, he will conceive of a higher temperature's sending the reaction in the direction of 1—if he prefers the second explanation of increased carbon dioxide production, then he will have no difficulty in seeing that a higher temperature would hasten the decomposition of acid oxalates.

There yet remains a very important fact to consider—namely, that acetone is oxidized by neutral permanganate at all times. Denis,[1] although she reports the production of carbon dioxide, oxalic and acetic acids from the action of acetone in a neutral permanganate solution, explains why "acetone will not be attacked by neutral permanganate." Witzemann[1] quotes this explanation: No isoacetone molecules are present in a neutral solution of acetone (three proofs of this are given—the most obvious is that acetone gives no precipitate with mercuric salts while the addition of a minute quantity of alkali causes the precipitation of mercuric isoacetone) and the permanganate will not attack normal acetone molecules. If acetone is oxidized by "neutral" permanganate as we found it to be, then one of two things must be true: either the acetone molecule itself is attacked or—what is more likely—there are present even in neutral solutions of acetone, some isoacetone molecules though not enough to reach the solubility product of mercuric isoacetone.

5. Summary.

1. Acetone is oxidized in both neutral and alkaline solutions of potassium permanganate to acetic acid, oxalic acid and carbon dioxide.

2. An increase in the initial alkali concentration and in the temperature increases the speed of the reaction.

3. The rate of the addition of the acetone solution affects the relative amounts, but not the character, of the reaction products.

4. As the initial alkali content of the samples increase, the amounts of oxalic acid increase until it reaches a maximum point. This maximum effect is produced when the alkali content is approximately seven grams per liter.

5. The amounts of acetic and carbonic acid grow less as the initial alkalinity value increases, until a minimum effect (also corresponding to an alkalinity value of seven grams per liter) is reached.

6. An increase in the temperature of the samples increases the yield of oxalic acid and of carbon dioxide and diminishes the yield of acetic acid. In samples whose initial alkali content is below seven grams per liter the differences produced by a change of temperature in the carbon

[1] *Loc. cit.*

dioxide and acetic acid yields is considerable, in samples whose alkali content is above seven grams per liter, very small, but constant.

7. The logarithms of the amounts of acetic, carbonic, and oxalic acids are, within limits (from 0.5 to 3.18 g. KOH per liter of solution) linear functions of the logarithms of the initial alkali concentration.

III. THE OXIDATION OF BUTYL COMPOUNDS

Three butyl compounds—the normal alcohol, aldehyde and acid were oxidized. The purpose of oxidizing the butyl alcohol was, as in the case of acetone and isopropyl alcohol, a three-fold one: to determine the effect of increasing alkali concentration upon the character and amounts of the oxidation-products; to determine the effect of increasing temperature upon the character and amounts of the oxidation-products; and to ascertain the successive steps in the reaction. The butyraldehyde and butyric acid were oxidized mainly to discover whether or not the speeds of reaction were affected by the rates of their respective additions to the alkaline permanganate solutions.

Experimental Part

1. Materials.—Butyl alcohol. The alcohol used was from the Eastman laboratories. It boiled at 116.9° C. (Beilstein, 116.88 (Kor.) and had a specific gravity of 0.8095). $\left(\text{Beilstein } 0.8099 \text{ at } \frac{20^\circ \text{ C.}}{20^\circ \text{ C.}}.\right)$ Owing to the high insolubility of the alcohol in water, the titrations were made with pure alcohol.

Butyraldehyde and butyric acid from the Eastman laboratories were used. The butyraldehyde boiled at 72.5° C. but the temperature continued to rise to 77° C. (Olsen—B. P., 73°–74° C.) The butyric acid began to boil at 150° C. and rose to 165° C. The distillate which came over between 160°–165° C. was used, (Olsen—B. P. 162°–3° C.). Titrations were made with the pure, rather than solutions of, the butyraldehyde and butyric acid.

All the other reagents used were made up as described under "Isopropyl alcohol."

2. Methods.—Much time was spent in trying to devise a method for the separation of the fatty acids whose presence in the reaction-mixtures was considered probable. The literature suggests several methods for the separation of fatty acids but none of these methods are quantitative. The following procedure gave good results for the determination of acetic acid and butyric acid in a mixture of the two:

Known quantities of acetic and butyric acids were made up to the mark in a volumetric flask. An aliquot portion was titrated with KOH solu-

tion. Another aliquot was boiled in a reflux condenser for half an hour with about 5 grams of freshly precipitated ammoniacal silver oxide. The mixture was filtered while hot and the filtrate received in weighed dishes. The solution was evaporated at 35°–40° C. and the resulting crystalline residue weighed and calculated.

By the use of this method 99.72 per cent and 99.75 per cent yields were obtained from an acetic acid solution and butyric acid solution respectively. When the two are present in a mixture the amounts of each are calculated by the "Indirect Method."

The separation of butyric and acetic acids by means of curves obtained by plotting the refractive indices of solutions of various acid content against the per cent of acid content, was tried. To test the practicability of this method ten samples of butyric acid solution ranging from 1 per cent to 0.1 per cent strength were made up and tested with the Zeiss refractometer. The 1 per cent sample (representing the probable maximum acid content of samples from the reaction-products) gave a reading of 18.0; the 0.10 sample a reading of 15.3. Pure water gave a reading of 15.0. This range of 27 points was entirely too small to make the method a practical one and the method was abandoned.

Tests were made on the ten samples mentioned above with the Westphal balance but once again the range between the density of the strongest sample and the weakest one was too small to be considered as a basis for making quantitative determinations.

In order to be sure that the substance calculated as oxalate was oxalate and not a succinate, an aliquot of the reaction-mixture was boiled with an excess of acetic acid (to remove CO_2O, treated with NH_4OH and finally with acetic acid to faint acidity. A solution of calcium acetate was added, the resulting precipitate filtered on an ashless filter treated with a few drops of sulfuric acid and weighed as calcium sulfate. Another aliquot of the same volume was treated under the same conditions with Calcium acetate. The precipitate in this case was dissolved in acetic acid and the solution titrated with a permanganate solution. The amount of calcium present in the calcium sulfate was 0.649 gram. The amount of calcium needed to unite with the "oxalate" found by the permanganate method was 0.651. The fact that these results check fairly well makes it certain that no succinic acid was present. Cahen and Hurtley[1] when they oxidized sodium butyrate with hydrogen peroxide found fifty per cent of the theoretical amount of succinic acid present. H. Dakin[2] reports no trace of succinic acid from an oxidation of ammonium butyrate with hydrogen peroxide or does E. J. Witzemann[3] from an oxidation of butyric

[1] Biochem, *Jour.*, **11**, 164 (1917).
[2] *J. Biol. Chem.*, **4**, 77 (1908).
[3] *Ibid.*, **35**, 83 (1918).

acid in alkali solution with hydrogen peroxide. (The point of these references is apparent when we remember that butyric acid is undoubtedly present in a solution of butyl alcohol undergoing alkaline oxidation.)

The oxidation itself was made in much the same manner as that of acetone and isopropyl alcohol. All oxidations were made at 50° C. At first about ten drops of the pure reducing material was added every fifteen minutes. Later this rate was varied in order to note the effect which varying speeds of addition had upon the amounts required for complete oxidation.

An experiment was made in which the order of addition was varied. A carefully weighed sample of butyl alcohol (about 9 grams) was dissolved in a liter of water and to it was added solid permanganate, a one-half gram at a time until the solution remained pink after standing over night.

3. Results.—The "neutral" solution of permanganate was faintly alkaline at the end of the oxidation. It showed traces of carbon dioxide and oxalic acid, and yielded large amounts of volatile acids. Tests were made on it for the aldehydes but the results were all negative. Carbon dioxide, oxalic acid and volatile acids were found in all the alkaline samples.

The most striking result and the one which finally led to the abandonment of the butyl compounds as reducing agents was this: it was impossible to duplicate results in titrating. A sample containing 5.32 g. KOH, for instance required 9.56 cc. of alcohol at one run; a similar sample titrated under precisely the same conditions of temperature required 9.99 cc.; another sample 8.26 cc.; and another 8.94 cc. The same variations were noted when butyraldehyde and butyric acid were used as reducing agents. Observations led to the belief that this difference was due to a difference in the rate of addition. To test this point two samples of permanganate solution were titrated with the alcohol at different rates of speed and two with butyraldehyde. Below are the results:

Reducing agent	Rate of Addition		
Alcohol	5 drops—15 min.	6.13	1.866 g.
Alcohol	5 drops—60 min.	4.50	1.970 g.
Aldehyde	5 drops—15 min.	5.50	2.276 g.
Aldehyde	5 drops—60 min.	4.75	2.237 g.

It is obvious from the above that the rate of addition affects not only the amounts of reducing material required but also the amounts of the products obtained. The titration of a sample required from thirty-six to forty-eight hours, making it necessary for the solution to stand over night. It was impracticable therefore to standardize the rate of addition without adding the alcohol so rapidly that the temperature was raised considerably. Work on the butyl compounds was therefore suspended until further investigations were made on rate of reaction.

Below are given the results from some of the solutions titrated:

0	14.96	0.074	0.005		
5.32	7.27	1.084	0.439	6.825	87.7
10.64	6.83	1.220	0.658	6.342	89.7
21.28	5.87	1.368	0.785	5.096	88.5
42.56	5.27	1.533	0.852	4.400	89.3
85.12	4.99	1.868	0.914	3.108	76.0
85.12	3.66	1.971	1.003	2.260	86.3
170.24	4.71	1.981	1.012	2.749	75.7

These results show that increasing initial alkali concentration up to at least 85.12 g. KOH per liter affects the amounts of the oxidation products.

A preliminary examination of butyric acid showed that it decomposed very rapidly in a strongly alkaline solution of permanganate. When alkaline permanganate solutions were titrated with butyric acid, the oxidation proceeded much more slowly than similar oxidation of butyl alcohol or of butyraldehyde. Moreover when a small amount of solid permanganate was added to samples in which the reaction was apparently complete, the color would disappear after a day or two. Reaction solutions of the alcohol and permanganate were tested in this way with the same results, that is, successive portions of additional permanganate were oxidized slowly. One sample consumed more than 5 grams of the permanganate in this way although it required thirteen days for it to lose its color after the last addition was made.

These results suggest one reason why the amount of alcohol required to reduce a given quantity of permanganate varies with the rate of addition. Either the butyric acid itself or some intermediary product is oxidized at an exceedingly slow rate.

The effect produced by changing the order of the addition of the oxidizing and reducing agents was very marked. 30 grams of permanganate (5.32 g. KOH per liter) required 9.27 grams of alcohol before its reduction was complete. 7.27 g. of butyl alcohol (5.32 g. KOH per liter) required 43.271 g. solid permanganate in order to completely oxidize it.

Summary

1. Butyl alcohol in a neutral solution of potassium permanganate yields volatile acids and traces of oxalic and carbonic acids.

2. Butyl alcohol yields volatile acids, oxalic and carbonic acids when oxidized with alkaline potassium permanganate.

3. Butyraldehyde and butyric acid are oxidized by neutral and alkaline potassium permanganate.

4. The amounts of oxalic and carbonic acids produced from butyl alcohol vary directly with the initial alkali concentration, the amounts of volatile acids produced vary inversely with initial alkali concentration. The change with varying alkali concentration reaches a maximum when that concentration is about 100 grams KOH per liter.

5. The amount of reducing agent required varies inversely with the speed of its addition.

6. The amount of butyl alcohol required to reduce a given amount of permanganate as well as the amounts of the oxalic acid produced is greatly affected by the order of addition.

It is a real pleasure to acknowledge my indebtedness to Dr. William Lloyd Evans for his unfailing inspiration and encouragement. I desire also to thank Professor Charles A. Foulk who very generously allowed me the use of his laboratory, and to express the deep sense of appreciation which I feel toward the memory of Professor Arthur Marion Brumback, my Chemistry teacher at Denison University. His was the initial stimulus that gave rise to my entire work in Chemistry.